

ARMY RESEARCH LABORATORY



Lithium Batteries: Present Trends and Prospects

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13. ABSTRACT (Maximum 200 words) This review discusses the objectives for both commercial and military batteries, the various options available for several types of lithium batteries, and the specific problems associated with each of the battery components (anode, cathode and electrolyte). While metallic lithium is the most desirable anode material for achieving very high energy densities, safety concerns have resulted in the development of new chemistries involving lithium-intercalating anode materials such as carbon and graphite which form the stable intercalate LiC ₆ . For cathode materials, research on the use of electrodes of the second kind (e.g. metal halides) has essentially been abandoned in favor of lithium-intercalating materials such as the transition metal oxides. Present day research is focusing upon the three oxides LiCoO ₂ , NiCoO ₂ and LiMn ₂ O ₄ . While the cobalt oxide presently appears to be the superior material and the nickel oxide is second to cobalt oxide, both environmental and economic factors are the bases for attempts to develop alternative cathode materials. These concerns are the driving forces for world-wide efforts to improve the electrochemical characteristics of the less energetic manganese oxides. The third area of concern is that of the electrolyte. The three major problems associated with liquid electrolytes which are discussed in detail are reactivity with the anode, reactivity with the cathode, and low conductivity.				
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INTRODUCTION

It is well known that the development of high energy density batteries has not kept pace with the rapid developments in the fields of portable electronic devices and in power and traction systems. It is also widely believed that the solution to the battery problem lies in development of a lithium battery. The question of "Why Lithium?" has three relatively simple answers. One reason why lithium-based systems are so attractive is dramatically shown in Fig. 1 where we compare the energy densities in Wh/kg and in Wh/L for various battery systems. The range of energy densities

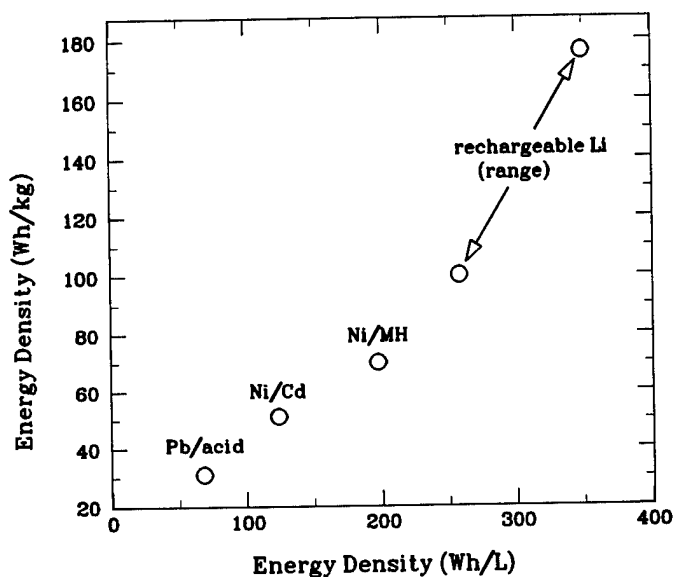


Figure 1. Energy density comparisons for various battery systems

for Li batteries is based on the specific system (i.e., use of metallic Li or lithiated carbon anodes), the type of cathode, and the electrolyte. These properties are the bases of the present review and are discussed in detail below. Given these high energy densities, lithium batteries could provide sufficient energy and power for electric automobiles enabling extended ranges of ≥ 290 km before recharging is necessary. A practical example is the primary lithium-SO₂ battery now in use by the military throughout the world which has enabled mission times to be increased by at least a factor of 10: in portable communication applications, original mission times from 1-2 h using an aqueous Zn-MnO₂ system have been increased to close to 10 h. Rechargeable Li-ion cells introduced by Sony in 1991 have more than doubled the operating times of portable equipments such as camcorders and laptop computers.

Another very significant driving force for the development of commercial rechargeable lithium batteries is simply one of economics. In 1994 it was estimated the total world-wide battery market was in excess of USD 25 billion, and a growth rate of at least 10 % per year was estimated well into the next century (1). While lead-acid batteries constitute a major fraction of the battery market, probably close to half, replacement of the Pb-acid battery with a lithium battery is a key goal for numerous research efforts, for example in the US by the Automotive Battery Consortium (USABC), Ray-o-Vac, Saft-America and Duracell, in Japan by the Lithium Battery Energy Storage Technology Research Association (LIBES), in Canada by Hydro-Québec and Moly-Energy, in Europe by Saft and Varta, and in Israel by Tadiran.

A third major driving force for development of rechargeable Li batteries relates to environmental hazards. In principle, a rechargeable Li-battery can be environmentally benign compared to the lead-acid battery, but additional problems exist relating mainly to safety which is discussed below.

The objectives for rechargeable Li-batteries for military applications are in fact similar to those for commercial applications such as those for electric vehicles, but with some minor differences as indicated in Table 1. The major differences between these objectives lie in the need for military

Table 1. Comparisons of performance objectives for military and commercial applications

	military (portable electronics)	military (high power)	commercial (electric vehicles)
energy density: Wh/kg	>100	>200	180
energy density: Wh/L	~150	~400	360
power density: W/kg	>50	>50	≥50
cycle life	>200	>35	≥500
cost: USD/kWh	< 1000	< 2500	100 - 400
temperature range	-40 to 70°C	0 to 50°C	ambient

equipments to operate over a wide temperature range, and for high power applications, the energy density requirements are somewhat more severe. Note that for commercial application to a full size electric automobile requiring a 40 kWh battery, the total cost of this battery will range from USD 4000 to USD 16000, with the more realistic value probably closer to the latter. This initial high cost of an electrochemical power source for automobiles (including subsequent costs of recharging these systems), must be weighed (compared) against the cost of liquid fuels over the lifetime of the

vehicle. Additional and most important basic issues which must be considered for commercialization are battery reliability and safety.

ANODES

Present technology for ambient temperature rechargeable cells is focusing on two types of anodes, metallic lithium and lithium-intercalating carbon materials:



and



The anodic reaction [2] represents the first carbon-coke material introduced by Sony in 1991 (2). Both metallic lithium and lithiated carbon materials are extremely reactive with organic solvents, and the apparent stability is due to the formation of passivating films. For metallic lithium, growth of this film results in continuing isolation of lithium upon cycling which severely decreases cycle life as cycling efficiencies can fall well below 70 %. A major advance in the improvement of lithium cycling efficiency was first reported some years ago by Slane et al. (3-5) who found that additions of a dialkyl carbonate such as dimethylcarbonate (DMC) and diethylcarbonate (DEC) to the electrolyte solution increased the lithium cycling efficiency to greater than 80 %, and further additions of CO_2 increased the cycling efficiency to greater than 98 % (4). Considerable research on DMC and DEC as well as CO_2 additions to various electrolyte solutions are important advances which are presently being further studied in a number of laboratories (6-8), and the beneficial effects of these additions are attributed to the formation of compact and highly stable films of LiCO_2 , HCO_2Li and various lithium alkoxides such as LiROCO_2 (4, 6). In spite of these advances, use of metallic Li as the anode material is of great concern to the battery industry due to continuing problems associated with dendrite formation, low cycle life, and safety. While the use of metallic lithium (melting point 180°C) certainly represents a serious safety hazard in instances of thermal runaway, the present authors are of the opinion that other battery components are of equal or greater safety hazards depending upon the nature of the solvent and, to a lesser extent, the electrolyte. To support this opinion, Fig. 2 is cited where it is seen that slowly increasing the temperature in sealed primary Li-MnO_2 primary cells with $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ electrolyte can lead to thermal runaway caused by reaction of the cathode with the electrolyte solution (9). Note that this thermal runaway initiated by reaction between the cathode and solvent starts at temperatures well below the melting point of lithium. While the present author is unaware of comparative studies for cathode materials

designed for rechargeable cells, it is clear that the reaction between the cathode and solvent is one of great concern.

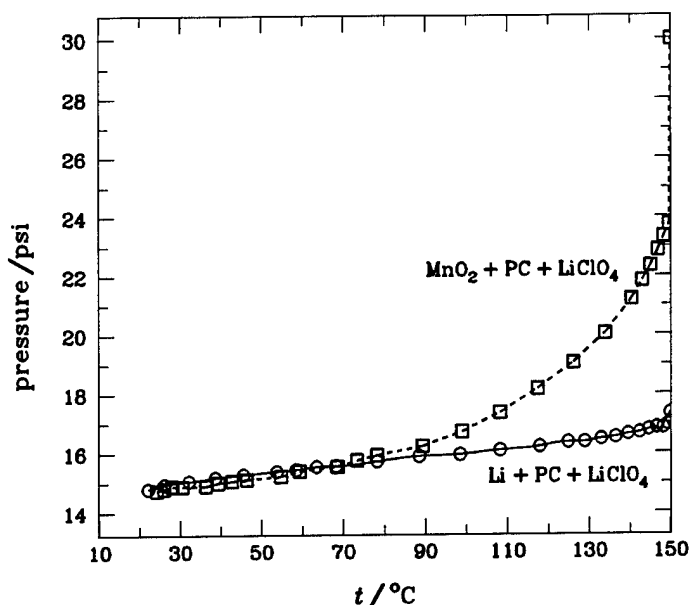


Figure 2. Temperature-pressure behavior of components of a primary Li-MnO₂ cell.

The dendrite problem associated with use of metallic Li anodes may indeed constitute a factor leading to shorts and temperature increase which in turn can initiate the electrolyte-cathode reaction. Such shorts can also lead to local heating and melting of lithium. For these reasons and since it appears that lithium intercalating anodes are more reversible upon cycling than metallic lithium, the battery community is now focusing upon lithium-intercalating cathodes such as carbon as given in eq. [2]. Cells based upon both anode and cathode intercalating materials are commonly referred to as “rocking chair” cells (e.g., see 10 for one of the first studies in this area and 11 and 12 for recent reviews). In rocking chair lithium-type cells, lithium ions are simply reduced/oxidized at specific cathode/anode intercalating materials thus circumventing the use of metallic lithium. Examples of overall cell reactions for Li-based rocking chair cells utilizing carbon and TiS₂ as anodes and a LiCoO₂ cathode are



and



While cells based on Li_xTiS₂ anodes are highly reversible and are stable in a number of electrolyte systems such as ionically conducting polymers (13) and in aggressive solvent systems such as acetonitrile (14), it is clear that the higher molecular mass of this anode is a disadvantage compared

to anodes based on metallic lithium. Carbon has long been known to intercalate various neutral and ionic species (15) depending upon numerous variable parameters. In general, carbons can be classified as either soft (i.e., graphitizable) or hard (nongraphitizable no matter how high its temperature treatment), and it exists in a variety of structures depending upon the nature of the carbon precursor and heat treatment conditions. The structure of graphitic carbon heated to very high temperatures in excess of 2000 K is well known as shown in Fig. 3A which represents the “saturated” species LiC_6 .

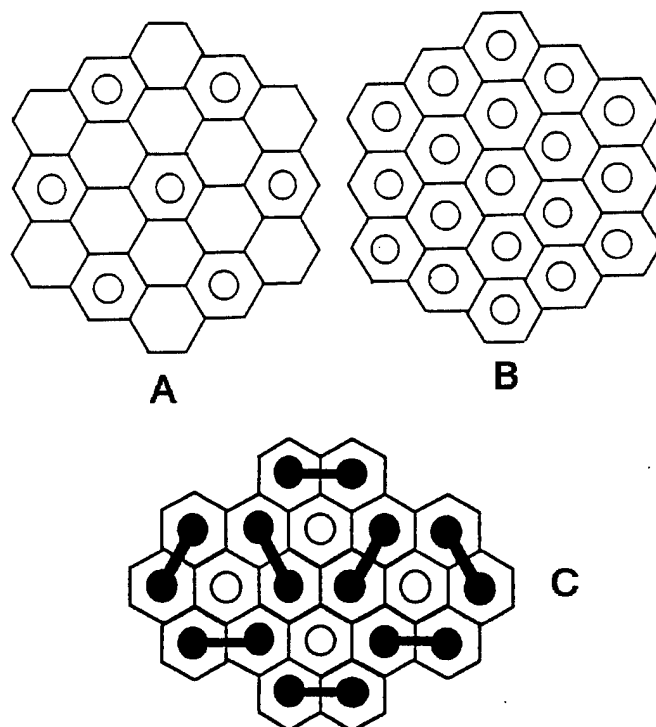


Figure 3. Li-C in-plane lattices. Open circles are ionic lithium and solid circles are covalently bound lithium. (A) LiC_6 : (B) “super dense” LiC_2 : (C) PPP-based graphite LiC_2 .

Upon intercalation, there is a transfer of charge from the Li 2s electron into the carbon ring, and $\text{Li}^{\delta+}$ resides between carbon layers. Due to Coulombic repulsion the lithium ions occupy symmetrical sites centered on second neighbor hexagons as shown in Fig. 3A. This structure corresponds to the stoichiometry of LiC_6 with a maximum theoretical capacity of 372 mAh/g. Practical cells based on both these hard and soft carbons and graphites will reversibly intercalate and deintercalate lithium at capacities at around 200 mAh/g (carbons) or upwards to 300 mAh/g or greater for some graphites. If additional lithium ions could be centered about each of the vacant hexagons shown in Fig. 3A, the resulting stoichiometry will be LiC_2 as shown in Fig. 3B. This “superdense” lithiated carbon has indeed been synthesized from metallic Li and highly orientated pyrolytic graphite at temperatures of 300-350°C and pressures of 30-60 kbar, and its theoretical

capacity was calculated as 1116 mAh/g (16, 17). However, this fairly dense material is unstable, and at atmospheric pressure and room temperature it decomposes rapidly to a metastable $\text{LiC}_6 + \text{LiC}_2$ material corresponding to a stoichiometry of $\text{LiC}_{3.8}$ (18). When the graphite is substituted with boron (0.5 atomic %), the lithiated material decomposes slowly to a metastable material corresponding to $\text{LiC}_{2.2}$. Subsequent to this initial decomposition, both the unsubstituted and boron-substituted metastable $\text{LiC}_{3.8}$ and $\text{LiC}_{2.2}$ phases remain virtually unchanged at room temperature and atmospheric pressure for periods greater than three months, but both eventually revert to LiC_6 (18). While electrochemical cells with these materials have not yet been studied, it appears that future research to improve the stability of this material would be fruitful for both primary and secondary lithium cells.

Another approach towards synthesizing high density and highly lithiated graphites has been reported by Sato et al. (19, 20), and by Dahn et al. (21, 22). Starting with the precursor *p*-poly(phenylene) (PPP) synthesized by ambient temperature polymerization of benzene (23), Sato et al. (19, 20) reported that graphitization at 700°C in a hydrogen atmosphere produces a highly disordered graphite with high hydrogen content (atomic H/C ratio = 0.24). Upon electrochemical lithiation another dense lithiated carbon corresponding to LiC_2 is produced as represented in Fig. 3C. In this figure, the open circles in each hexagon represent $\text{Li}^{\delta+}$, and the solid circles represent, according to Sato et al., lithium covalently bonded as Li_2 . The maximum theoretical capacity of the graphite synthesized by Sato et al. is 1160 mAh/g. Dahn et al. (cited in ref. 22) have also produced a non-graphitic carbon (i.e., a “hard” carbon) of lower H/C ratios which appears to involve lithium covalently bonded to hydrogen with a maximum theoretical lithium capacity of 740 mAh/g. The electrochemical intercalation and deintercalation of the PPP-based graphite is shown in Figure 4. This figure compares the capacities for the second cycles of the PPP-graphite produced by heat treatment at 700°C in a hydrogen atmosphere to that of the PPP-graphite produced by heat treatment at 1500°C in an inert atmosphere. For the former graphite, the experimental capacity upon discharge to a cutoff voltage of 3.0 V vs Li/Li^+ is around 695 mAh/g, and for the latter the capacity is around 372 mAh/g (19).

While the graphite of high H/C content reported by Sato et al. appears to degrade upon cycling, it is clear that we are approaching a stage where new carbons are being produced which can reversibly

intercalate lithium at capacities greatly exceeding 350 mAh/g. In fact the capacities obtained by some of these new carbon materials are not that far removed from those obtained with metallic

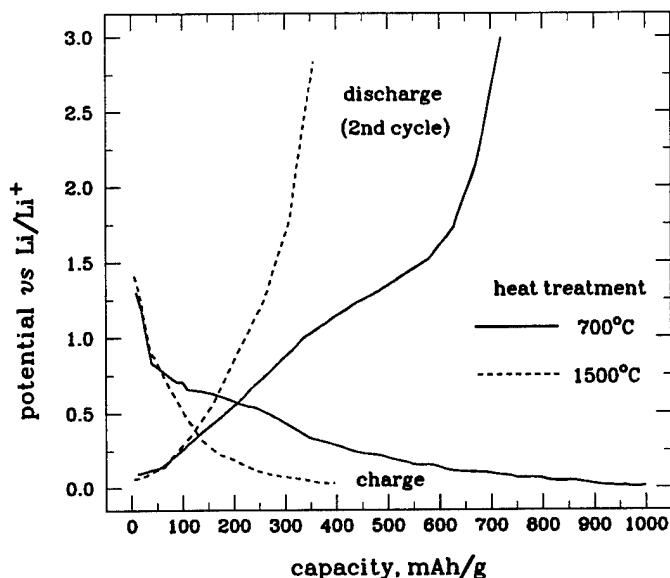


Figure 4. Second cycle charge-discharge curves for PPP-based graphites (from ref. 19).

lithium as shown in Table 2. The important item to note in this comparison is that due to capacity loss upon cycling, rechargeable lithium cells based on metallic Li require at least three to four times excess lithium to the requirements, particularly the cycle life, specified in Table 1 above. The practical capacities realizable in rechargeable cells based on carbon anodes and metal oxide cathodes is highly dependent upon the cutoff voltage selected for charging. In the commercial Sony

Table 2. Comparisons of various lithiated carbons

anode material (type)	temperature of preparation ($t/^{\circ}\text{C}$)	mAh/g theoretical	mAh/g practical
pitch coke (hard)	>2000	372	170 ^a
PPP-graphite (LiC_6)	1500	372	200-300 ^{b,c}
PPP-graphite (LiC_2)	700	1160	350-550 ^{b,d}
hard carbon (low H/C ratio)	≤ 1000	740	?
graphite-high pressure preparation (LiC_2)	300-350 $^{\circ}\text{C}$ (30-60 kbar)	1116	not determined
metallic lithium		3860	900 to 1300 ^e

^a E.g. the pitch (petroleum) coke as used in the Sony cell (2)

^b Based on a cutoff voltage of 1.5 to 2.0 V vs Li/Li⁺.

^c 372 mAh/g obtained on cycle N^o. 2 to a cutoff voltage of 3.0 V (see Fig. 4).

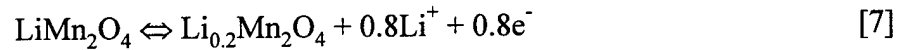
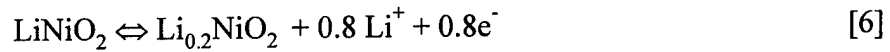
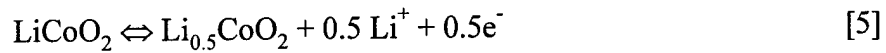
^d 695 mAh/g obtained on cycle N^o. 2 to a cutoff voltage of 3.0 V (see Fig. 4).

^e Based on 4 to 3 times excess lithium (~ 800 mAh/g based on 5 times excess Li).

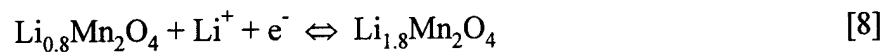
cell based on coke LiC_6 , the cutoff charging voltage is 4.1 V, but we have found that charging to 4.25 V leads to an initial increase in capacity of around 16% with no apparent safety problems: however the capacity fades more rapidly upon cycling than cells charged to 4.1 V (24). On the other hand, our experience with Li-ion cells which employ graphitic carbons (LiC_6) is that they do present a serious safety hazard when charged beyond 4.2 V: violent and unpredictable venting was observed upon the nail penetration test and to a lesser extent, upon crushing. Reducing the charging cutoff voltage to 4.1 V significantly reduces these safety hazards.

CATHODES

At present, the major candidates for cathode materials for continued development of high energy density rechargeable lithium batteries are the oxides LiCoO_2 , LiNiO_2 and LiMn_2O_4 . The cathodic reactions of interest for these materials, eqs. [5 - 7], indicate that the useful capacity is limited as



complete deintercalation is generally not possible due to irreversible phase changes in these materials. For example, the initial studies on the reversibility of Li_xCoO_2 showed that between the regions of $0.5 \leq x \leq 1$, there are three reversible phase transitions; there is also a fourth but irreversible phase for $x < 0.5$ where the layered rock-salt structure of Li_xCoO_2 is destroyed (4). This limits the charge/discharge potentials to a range of around 4.5 V to 3.0 V vs Li/Li^+ . Similar complexities in phase transitions are observed for Li_xNiO_2 which limits x to around 0.2 to 0.3 (25). While cells for commercial applications based on nickel oxides offer distinct advances over cobalt-based systems (cost, environment), our findings that LiNiO_2 cells exhibit severe rate limitations below 0°C may limit its use for military applications. The useful potential range of LiMn_2O_4 cathodes is between 4.5 V and 3.5 V (see Fig 5 below). Although there is a second reversible region between 3 V and 2.5 V in which x in $\text{Li}_{0.8+x}\text{Mn}_2\text{O}_4 \approx 1$,



the phase transition to $\text{Li}_{1.8}\text{Mn}_2\text{O}_4$ is less reversible compared to the 4 V discharge region, and in view of its low potential (discharges at ~ 2.5 V) and capacity fade upon cycling, this second region is

not considered useful for rechargeable battery applications: applications to primary lithium batteries are certainly of interest. A comparison of the first cycle discharges for the three cathode materials is shown in Fig. 5 which was taken from a previous review (12). Both LiCoO_2 and LiNiO_2 show moderately high capacities (180 to 200 mAh/g) on the first cycle, whereas LiMn_2O_4 yields a somewhat lower capacity of 137 mAh/g.

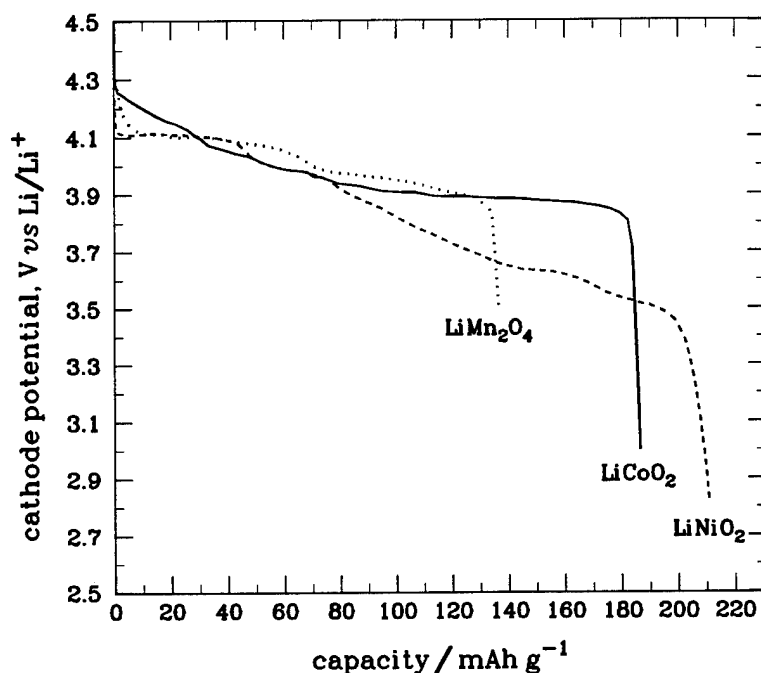
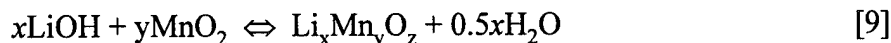


Figure 5. Comparison of first cycle discharge at 0.1 mA cm^{-2} of LiCoO_2 , LiNiO_2 and LiMn_2O_4 cathodes at room temperature. The electrolyte is $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in EC-PC (ref. 12).

In addition to its lower initial capacity, $\text{Li}_x\text{Mn}_2\text{O}_4$ capacities fade significantly upon cycling (see Fig. 6) due primarily to a phase transition at $\sim x = 0.5$ (26). However, in view of being environmentally “friendly” and its low cost compared to LiCoO_2 and LiNiO_2 , there remains great interest in improving the cycling behavior of LiMn_2O_4 . Since the structure of LiMn_2O_4 is quite sensitive to its method of preparation, considerable research is being carried out on structural modifications by various types of synthesis. The classical preparation of stoichiometric LiMn_2O_4 involves heating a mixture of LiOH and MnO_2 in air at temperatures above $\sim 800^\circ\text{C}$. Abraham (27) reported the use of lower temperatures ($\sim 400 - 450^\circ\text{C}$) which produces structures different from the spinel phases produced from the higher temperature preparation. For example, varying the ratio of LiOH/MnO_2 in the reaction



yields $\text{Li}_{0.9}\text{Mn}_2\text{O}_{4.2}$ and $\text{Li}_{1.0}\text{Mn}_2\text{O}_{4.7}$, the latter exhibiting almost complete utilization of lithium: i.e. an initial utilization of one mole of Li per 2 moles of Mn which fades to an almost constant 0.6 Li per 2Mn upon cycling. In another recent study, Guohua et al. (28) have prepared quaternary spinels which are oxygen deficient phases of $\text{LiM}_y\text{Mn}_{2-y}\text{O}_{4-\delta}$ ($M = \text{Co}, \text{Cr}, \text{Ni}$) by heating mixtures of Li_2CO_3 and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or MnCO_3 with the oxides Cr_2O_3 , $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or $\text{NiCoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Mixtures were heated in air to 750°C , and the spinel $\text{LiCr}_{0.167}\text{Mn}_{1.83}\text{O}_{3.83}$ shows excellent capacity retention compared to $\text{LiMn}_2\text{O}_{3.81}$ as shown in Figure 6. The operating voltage region for this specific Cr-Mn spinel is 4.45 V to 3.6 V at a current density of 0.2 mA cm^{-2} , and at

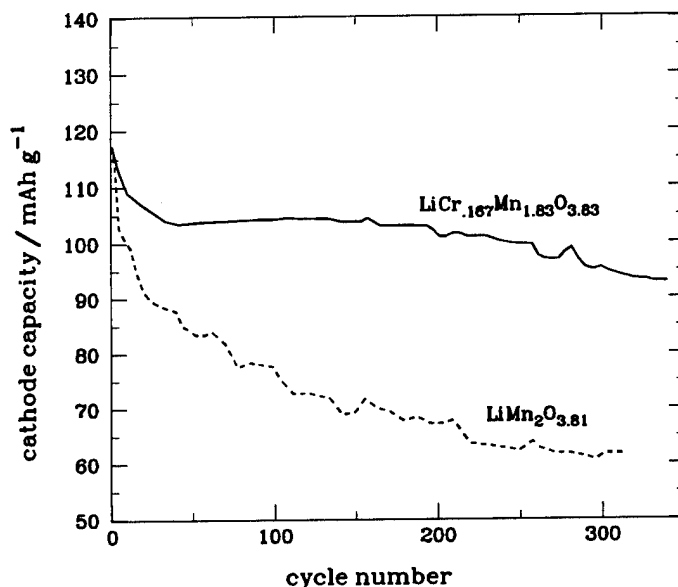


Figure 6. Capacity behavior upon cycling for $\text{LiMn}_2\text{O}_{3.81}$ and $\text{LiCr}_{0.167}\text{Mn}_{1.83}\text{O}_{3.83}$ at room temperature in $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ in PC. Cells charged and discharged at 0.2 mA cm^{-2} between the voltage limits of 3.60 to 4.45 V vs Li/Li^+ (28).

the end of 300 cycles its energy density was given as 370 Wh kg^{-1} . The improved behavior of the Cr-containing spinel was attributed to the increasing level of Mn^{3+} which results in a structure of enhanced stability (28). It is noted that the electrolyte used in these studies was $1 \text{ mol dm}^{-3} \text{ LiClO}_4$ in propylene carbonate. It appears at this time that continued research on structural modifications of LiMn_2O_4 spinels will result in a cathode material with energy densities and cycle lives comparable to cobalt and nickel oxides.

While still a scientific curiosity, the use of carbon materials for both anode and cathode in a rocking chair cell represents the ultimate for low cost systems. It has been known for some time (29-31) that carbons and graphites can intercalate anions according to the proposed (30) mechanism,



In this reaction, X^- can be any of the common anions used in Li battery studies such as ClO_4^- , BF_4^- , PF_6^- , etc., and where the value of n is dependent upon the nature of the carbon or graphite used, and the solvent. In Bennion's pioneering work (30, 31), it was reported that reinforced pyrolytic graphite (RPG) could be charged and discharged with nearly 100% coulombic efficiency in solutions of LiClO_4 in sulfolane and propylene carbonate. This graphite exhibits an OCV of around 4.5 V vs Li/Li^+ , and can be discharged at reasonable rates of 1-3 mA cm^{-2} with average potentials above 3.5 V. The problems reported by Bennion et al. relate to low cycle life due to disintegration of the cathode, and quite low capacities: i.e., a maximum capacity of 90 Coulombs per g of carbon (26 mAh/g) was found which corresponds to $n = 89$ in eq. [10]. Similar findings were reported by Ohzuku et al. (32), and in more recent studies Watanabe et al. (33) and McCullough et al. (34) reported improved capacities from ~200 mAh/g (34) to 398 mAh/g (33) depending again upon the solvent and carbon or graphite material employed. In view of the findings (35, 36) that in aqueous acidic solutions, n in eq. [10] reached values of 12 to 24, it appears to the present authors that anion-intercalating carbon materials could be a fruitful area for future research.

ELECTROLYTES

The successful development of a rechargeable lithium battery is heavily dependent upon the proper development of a suitable electrolyte system, the nature of which can vary significantly depending upon its stability towards lithium and the cathode of choice. In this review, we shall focus on two alternatives, namely liquid electrolytes (excluding molten salt systems) and solid state electrolytes (excluding inorganic electrolytes). Both types of electrolytes have their advantages and disadvantages which is not the objective of this review, but a few comments should be made in this respect. Liquid electrolytes have the distinct advantage of possessing high conductivities over a wide temperature range, but cells constructed with liquids must be hermetically sealed in metallic cases to prevent leakage and insure safety in the advent of excessive pressure buildup. Obviously, the sealing of cells employing solid polymer electrolytes is, in principle, simpler and less expensive which is a major reason why these systems are receiving considerable attention in laboratories throughout the world (e.g., see 37). A major drawback with polymer electrolytes is their low conductivities over a wide temperature range, and this is one area in which the present author has been active over the last several years. Both well known concepts regarding liquid and polymer

electrolyte systems are discussed along with a review of new and recent developments which appear highly promising.

Liquid Electrolytes. Research on rechargeable batteries has been an ongoing effort for around 35 years, probably beginning with the work of Harris (38) when it was realized the metallic lithium could be electrochemically deposited and dissolved in propylene carbonate. It is universally recognized that propylene carbonate used by itself results in cells in which lithium cycles poorly, and that use of solvent mixtures or "blends" offer a reasonable solution to this problem. Table 3 lists a number of aprotic solvents which have received attention over the years. In selecting a suitable solvent for use in rechargeable Li batteries, the ideal material should possess high thermal and high chemical stability towards anode and cathode, exhibit high solubilities for important electrolytes and nonelectrolytes, and exhibit high conductivities over a large temperature range, preferably with high lithium ion transport (the ideal electrolyte would have a lithium ion transport number of unity to prevent concentration polarization upon cell discharge). Similar requirements exist for the lithium salt itself: i.e., with regards to chemical and thermal stability, and mobility in aprotic solvents. These are the issues which are addressed below, and examples of recent successes in these areas are also briefly discussed and illustrated.

Initial attempts to develop rechargeable lithium systems proved difficult since the selection of aprotic electrolyte solutions exhibiting high stability towards electrochemical oxidation and reduction was often accomplished by systematic searches for suitable materials, starting with PC systems mainly due to their high dielectric constant and ability to dissolve large amounts of electrolyte. Solvents with low permittivities ($\epsilon \leq 15$) were initially avoided due to the high degree of ion association which was expected to result in poorly conducting solutions. However, use of solvents with low permittivities was actually found to be extremely conductive as shown in Fig. 7. In this figure it is seen that solutions of LiAsF_6 or LiClO_4 are much more conductive over a very wide temperature range in low dielectric constant solvents such as MF and MA than in PC. Conductivities in THF are known to be quite high, comparable to those in MF, and the low conductivities for 2Me-THF solutions is probably due to a decrease in electron density about the ether-oxygen due to the methyl group on the ring. The problem with use of MF is that lithium cycles poorly in its solutions, and the solvent appears to react (oxidize) at high potentials at cathodes such as LiCoO_2 (4). Li/LiCoO_2 cells perform better in MA solutions (39), but still significant

degradation was observed due to poor lithium cycling efficiencies and oxidation of the solvent at the cathode upon charge. In general, ethers and esters while highly conductive are problem solvents

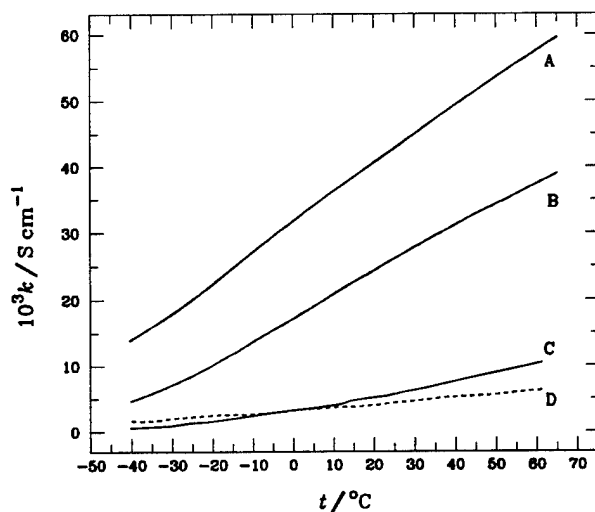


Figure 7. Electrolytic conductivities as a function of temperature (from ref. 4). (A) 2 mol dm^{-3} $\text{LiAsF}_6 + 0.4 \text{ mol dm}^{-3}$ in MF: (B) 2 mol dm^{-3} LiAsF_6 in MA: (C) 1.0 mol dm^{-3} LiClO_4 in PC: (D) 1.5 mol dm^{-3} LiAsF_6 in 2Me-THF.

due to their reactivities with both anode and cathode. In addition, possessing centers of high electron density leading to strong coordination with Li^+ , the possibility of co-intercalation of solvent upon cell discharge (transported with Li^+) can lead to structural decomposition of the metal oxide cathode. The introduction of alkyl carbonates as co-solvents (3-5), which stabilizes the protective film on Li anodes, into solvents used in present day research and development takes advantage of the beneficial effect of alkyl carbonate additions: e.g., the electrolyte in the Sony cell is LiPF_6 in a mixture of PC (70 volume %) and DEC.

The selection of the solvent(s) for use in rechargeable lithium cells presently focuses around PC and EC with and without additions of an alkyl carbonate, and/or with additions of a low viscosity solvent to insure adequate conductivities for the purpose for which the cell is designed (i.e. rate requirement) (40, 41). While improvements in solvent selection are still required, there exists the need for considerable improvement in the electrolyte. The chemistries of the various electrolytes presently under consideration are quite complex, and only a few representative examples are given below with brief discussions on their advantages and disadvantages.

One of the important problems to be considered is that related to thermal and electrochemical stability (i.e., safety), toxicity, and cost. LiClO_4 solutions while moderately conductive are subject to violent decomposition, particularly in ether solutions (42). While LiAsF_6 is one of the most

Table 3. Properties of selected solvents (25°C unless stated otherwise)

solvent	ϵ	η/cP	solvent	ϵ	η/cP
toluene	2.379	0.552	2-cyanopyridine (2CNP, 30°C)	93.77	1.832
dimethyl carbonate (DMC)	3.12	0.585	propylene carbonate (PC)	64.92	2.53
diethyl carbonate (DEC)	2.82	0.748	ethylene carbonate (EC, 65°C)	89.6	1.85
tetrahydrofuran (THF)	7.39	0.46	nitromethane (MeNO ₂)	35.99	0.6162
2-methyl-THF (2Me-THF)	6.20	0.457	dimethyl sulfite (DMSI)	20.80	0.8732
diethyl ether (DEE)	4.33	0.242	tetramethylene sulfone (TMSO, 55°C)	43.3	10.29
1,3-dioxolane (1,3-diox)	6.86	0.5969	dimethyl sulfoxide (DMSO)	46.68	2.016
dichloromethane (DCM)	8.93	0.41	acetonitrile	35.96	0.3426
dimethoxymethane (DMM)	2.71	0.329	dimethylformamide (DMF)	36.71	0.794
dimethoxyethane (DME)	7.15	0.402	γ -butyrolactone (γ -BL)	41.77	1.727
methyl formate (MF)	8.90	0.328	SO ₂ (0°C)	15.35	0.403
methyl acetate (MA)	6.67	0.368	water	78.40	0.8903

conductive electrolytes available, it suffers from thermal and electrochemical instability leading to the Lewis acid AsF_5 and the insoluble LiF . Environmental problems associated with the degradation products of LiAsF_6 is the major driving force for the search of alternative electrolytes. Lewis acids such as AsF_5 and PF_5 can initiate solvent polymerization resulting in rapid capacity loss upon cycling. In addition, LiPF_6 appears to undergo thermal decomposition in the solid state at around 30°C (43), and in solution decomposition appears to begin at around 130°C. $\text{LiCSO}_3\text{CF}_3$ (lithium triflate) is thermally and electrochemically highly stable, but it is highly associated in solution resulting in extremely poor (low) conductivities (e.g., see 41). The introduction of the highly stable imide salt lithium *bis*(trifluoromethanesulfonyl) imide, $\text{LiN}(\text{SO}_2\text{CF}_3)_3$ by Armand (44)

and the methide salt lithium *tris*(trifluoromethanesulfonyl) methide, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, by Dominey (45) appear to have major advantages over lithium salts of other anions. For example, they are extremely stable compared to AsF_6^- and PF_6^- , as demonstrated in Fig. 8 reported recently by Croce et al. (46). This figure shows an overlay of linear sweep voltammograms for the four lithium salts LiX (X = imide, methide, hexafluoroarsenate and hexafluorophosphate) at a Pt working electrode.

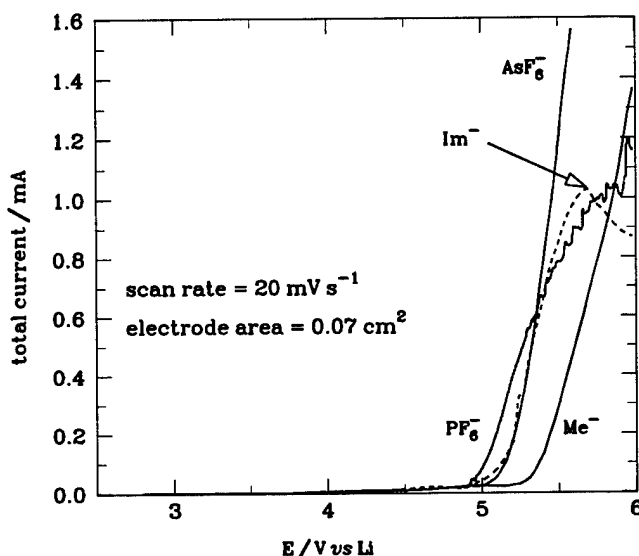


Figure 8. Linear sweep voltammograms for LiX in 1,2-dimethyl-3-propylimidazolium salts (i.e. Dmpix salts) at 80°C . $\text{X} = \text{AsF}_6^-, \text{PF}_6^-, \text{N}(\text{SO}_2\text{CF}_3)_2$ and $\text{C}(\text{SO}_2\text{CF}_3)_3$ (from ref. 46).

The electrolytes used in these studies are those based on the large organic cation 1,2-dimethyl-3-propylimidazolium (Dmp^+) with each of the four anions: i.e., DmpIm^+ , DmpMe^+ , DmpAsF_6^- , and DmpPF_6^- which are all liquids at 80°C . Using these liquid salts eliminates the problem of solvent oxidation since the anion of the salt LiX and the electrolyte Dmpix are identical, and the anodic limits shown in this figure are therefore true indications of the stabilities of each anion. The methide anion is clearly the most stable whereas PF_6^- is clearly the least stable. While Fig. 8 indicates the methide and imide anions are stable in these liquid organic salt solutions to potentials exceeding 5 V, in aprotic organic solvents the effects of solvent and substrate tend to lower these anodic limits. For example, the cyclic voltammograms (5 mV/s) in Fig. 9 show that in a 1 mol dm^{-3} $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ solution in a 50:50 mass % mixture of EC-DMC, the anodic limits do not exceed around 4.3 V depending upon the substrate (47). Aluminum, the support and electronic conductor most commonly used for metal oxide cathodes, is the most stable, whereas Pt and glassy carbon substrates lead to decomposition at lower voltages. Similar results have been obtained for the methide salt (47).

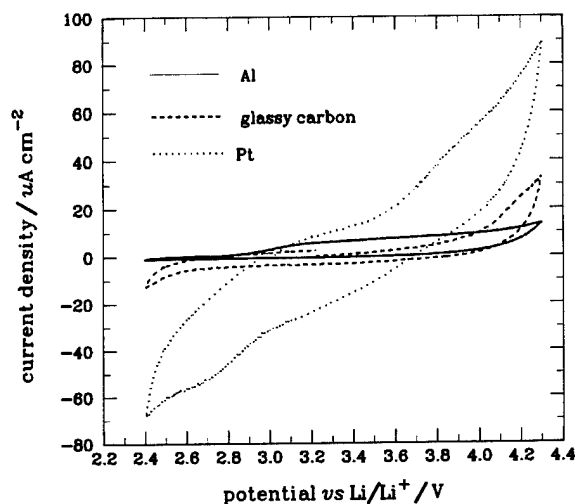
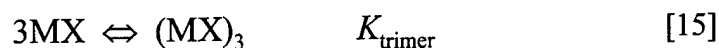


Figure 9. Cyclic voltammograms for $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in 50:50 mass % EC-DMC at 25°C on various substrates. Sweep rate is 5 mV sec^{-1} (47).

The conductivity behavior of lithium salts has been the subject of numerous reviews (e.g., 48 - 50) with the objectives of determining the basic properties of ion-solvent interactions which hopefully will serve as guides for continuing development of highly conductive, safe and stable systems. Fig. 10 is a representative example of one of the major problems concerning complex formation which results in solutions of abnormally low conductivities (from refs. 51 and 52). This figure not only demonstrates the superior behavior of LiAsF_6 , but it also indicates the complexities of solute-solvent interactions. The difference between LiAsF_6 and LiClO_4 is largely due to the greater ion association of the latter salt. The minimum in these curves is attributed to triple ion formation, and, at much higher concentrations approaching and exceeding 1 mole dm^{-3} (not shown in Fig. 10), a maximum is observed followed by a rapid decrease in molar conductivity. It is in these higher concentration regions that large increases in viscosity combined with formation of additional complexes such as neutral dimers and trimers (e.g., see 48) significantly decrease the conductivities. The complex equilibria which exist in low dielectric solvents can be summarized in eqs. [11 - 15].



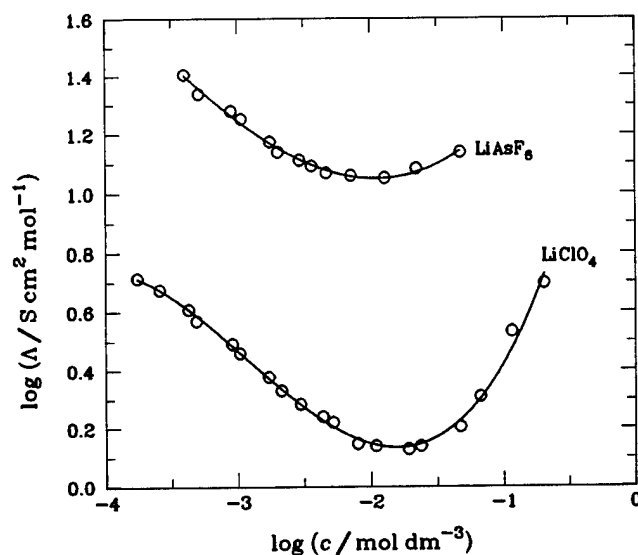


Figure 10. Molar conductivities in DME at 25°C (51, 52).

To eliminate neutral complexes which are a major cause of diminished conductivities, three approaches have generally been pursued. The first is the selection of a relatively high dielectric constant solvent such as PC or EC to minimize ion association, eq. [11], and to practically eliminate the remaining equilibria in eqs. [12 - 15]. Small additions of a low viscosity solvent (DME, DEC, MF, etc.) will lower the dielectric of the medium, and, providing this lowering is not too great, improved conductivities will result. Another approach to minimize K_a of course involves the development of new electrolytes as discussed above, and both the imide and methide salts are successful examples of this approach. Table 4 below compares the infinite solution molar conductivities of important lithium salts in selected solvents along with K_a values, with water included as a reference (46). Table 5 gives the derived cation transference numbers, t_+ , for the various salts listed in Table 4. In general, both the imide and methide salts undergo little ion association compared to the other salts, and this is attributed to the important properties of the large anions which contain covalent bonding which leads to significant charge delocalization. It is also important to note that the transference number for Li^+ (Table 5) is higher for the imide and methide systems due in part to the large size of these anions, and in part due to greater solvation of these anions compared to the smaller anions (46). It is concluded that the development of new salts based on large anions which exhibit significant charge delocalization constitutes a very fruitful area for future research. As a final example, the recent work of Barthel et al. (53) is cited: these authors report the synthesis of lithium *bis*[1,2-benzenediolato(2)-O,O']borate, $\text{Li}[\text{B}(\text{C}_6\text{H}_4\text{O}_2)_2]$, which was

found to be non-toxic, thermally, chemically and electrochemically stable, and inexpensive. Since the anodic limit of this salt is somewhat low (~ 3.6 V vs Li/Li⁺), fluorination of this borate anion is presently being investigated.

Table 4. Comparison of conductivity parameters at 25°C^a

	H ₂ O		PC		AN		DMF		MeNO ₂	
salt	Λ°	K_a	Λ°	K_a	Λ°	K_a	Λ°	K_a	Λ°	K_a
LiClO ₄	105.9	----	26.75	1.3	173.26	16.47	73.40	6.6	110.60	182.2
LiPF ₆			26.1	2.1						
LiAsF ₆	95.07	----	22.53	----	170.06	9.1	74.18	3.3		
LiIm	70.89	----	22.76	----	153.71	4.7				
LiMe	66.47	----	20.22	----	144.7	----	58.61	----	91.74	27.8

^a Λ° /S cm² mol⁻¹ and K_a /dm³ mol⁻¹. See ref. (46) for complete literature citations.

Table 5. Cation transference numbers, t_+° , at 25°C

salt	H ₂ O	PC	AN	DMF	MeNO ₂
LiClO ₄	0.365	0.307	0.403	0.323	0.388
LiPF ₆	0.395	0.314	0.405	---	---
LiAsF ₆	0.407	0.36 ₅	0.414	0.337	---
LiIm	0.546	0.361	0.455	---	---
LiMe	0.582	0.407	0.484	0.427	0.468

The minimization (hopefully the elimination) of ion association can be accomplished in a third fashion, namely by adding cation-coordinating ligands which strongly coordinate Li⁺ while simultaneously shielding the cation from contact with the anion. The addition of macrocyclic ligands, L, such as crown ethers, cryptands and polyamines which can effectively (strongly) coordinate Li⁺ results in solutions containing several complex species as shown in eqs. [16 - 17].



Ion association of the coordinated complex is generally much smaller than for the uncomplexed or “free” salt (see eq. [11]) as reported in our initial studies on these systems (54-56), and providing that the formation constant K_f is sufficiently large, the conductivity of these solutions is often

observed to increase upon addition of the macrocyclic ligand. An example of this effect is shown in Fig. 11 where solutions of LiBF_4 and LiSO_3CF_3 in PC are titrated with a solution of the crown

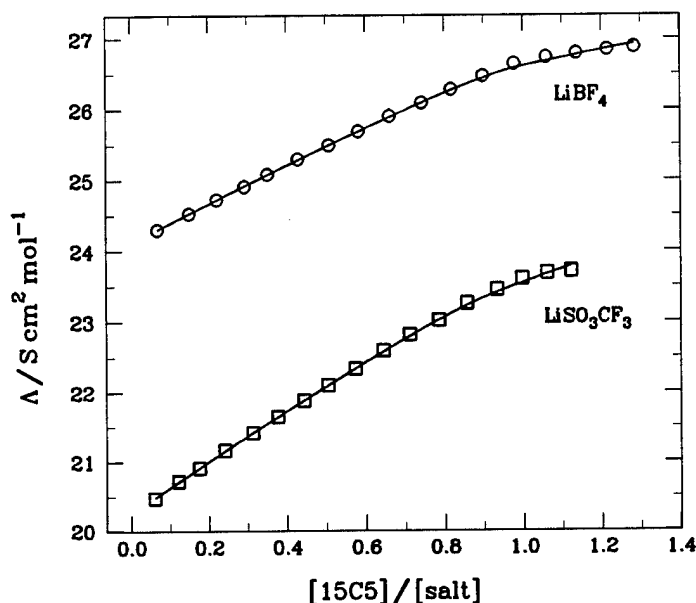


Figure 11. Conductometric titration of 0.05 mol dm^{-3} LiBF_4 and LiSO_3CF_3 solutions with 15C5 in PC at 25°C (from 57).

ether 15C5 (57). In addition to the effect of minimizing ion association (eq. [11]), the addition of macrocyclic ligands to Li salt solutions in PC or PC mixtures with DCM can also result in an increase in the cation transference number as indicated for PC solutions in Table 6. This table lists single ion molar conductivities at infinite dilution, λ° , in PC for a number of anions, Li^+ , and for Li^+ complexes with the crown ethers 12C4, 1-aza-12C4, 1-benzo-aza-12C4 and 15C5 (data from ref. 58). Similar results were also reported for 18C6 complexes in PC (54) and 2CNP (55), and for 18C6 and the cryptand [222] in PC mixtures with DCM (59). This unexpected result was attributed to solvation effects where the large solvation sphere of the cation is essentially completely removed as the cation enters the cavity of the macrocyclic ligand: i.e., the radius of the “free” but highly solvated Li^+ ion is greater than the radii of the Li^+ -ligand complexes. This effect appears to be highly related to ion-solvent interactions and hence solvent dependent: e.g., we do not observe this effect in solutions of the highly structured solvents methanol and acetonitrile (56). Aromatic compounds such as toluene and chlorinated solvents such as DCM are of interest since they are generally less reactive with lithium, have relatively low viscosities over a large temperature range, and are liquids over a large temperature range: the liquidus range for DCM is -95.1°C to 39.8°C , and for toluene the liquidus range is -95.0°C to 110.6°C . In view of the low salt solubilities in aromatic and halogenated hydrocarbons, mixtures with high dielectric constant solvents probably

constitute an important direction for future development (e.g., see 59) as does the utilization of complexing ligands to increase. For example, Whitney et al. (60, 61) reported that additions of the stable amine 1,1,4,7,7-pentamethyl diethylenetriamine (PMDT), $[(CH_3)_2N(CH_2)_2]_2NCH_3$, to toluene solutions not only greatly solubilizes lithium salts, but can also lead to conductivities sufficiently high for use as the electrolyte in lithium batteries. Whitney's conductivity results for 1.0 mol dm^{-3} LiBr in toluene and for 0.8 mol dm^{-3} LiAsF₆ in a 30:70 mole % TMSO:toluene mixture are shown in Fig. 12.

Table 6. Infinite dilution single ion molar conductivities of "simple" and complexed ions at 25°C.

Ligands are 12-crown-4, 1-aza-12C4, 1-benzo-aza-12C4, and 15-crown-5: solvent is PC.

CATION	$\lambda_+^0 / \text{S cm}^2 \text{ mol}^{-1}$	ANION	$\lambda_-^0 / \text{S cm}^2 \text{ mol}^{-1}$
Li ⁺	7.86	ClO ₄ ⁻	18.89
[Li ⁺ 12C4]	10.02	BF ₄ ⁻	20.71
[Li ⁺ 1-A-12C4]	10.25	CF ₃ SO ₃ ⁻	16.41
[Li ⁺ 1-B-A-12C4]	11.99	imide	14.9
[Li ⁺ 15C5]	10.50	methide	12.4

Solid state polymer electrolytes (SPE). First introduced by Armand (62), the inherent advantages of batteries utilizing an SPE have been the driving force for considerable research in this area. Three international symposia, several books and numerous publications have been devoted to these materials with particular emphasis on their ion transport properties and upon stability at the Li-polymer interface (37, 63, 64). The solubility of lithium salts in polymers is made possible by the presence of ether oxygens present either in the polymer backbone or in side-groups, and the ionic conductivity is confined primarily to amorphous regions where segmental motion of the polymer chains is responsible for ionic transfer. Conductivities, σ , are generally measured using ac-impedance techniques (the frequency-independent real part of the impedance (65)), and the temperature dependence of σ is generally found to follow some form of the Vogel-Tammann-Fulcher (VTF) equation

$$\sigma = AT^{-1/2} \exp\left\{\frac{E}{T - T_0}\right\} \quad [18]$$

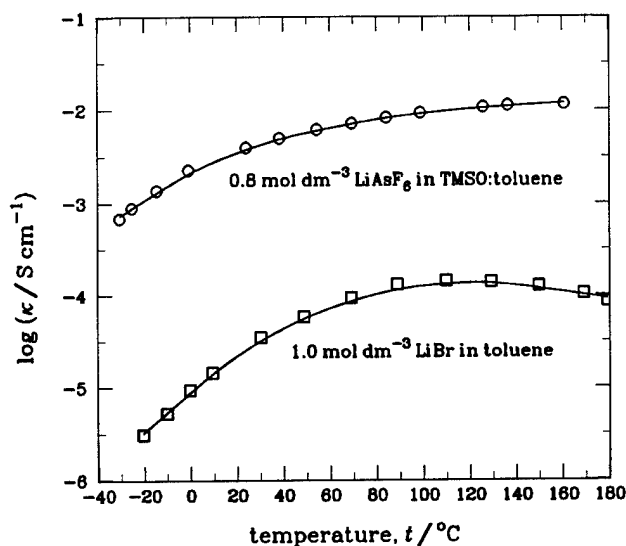


Figure 12. Temperature dependence of the electrolytic conductivities of 1.0 mole dm^{-3} LiBr + PMDT in toluene, and 0.8 mol dm^{-3} LiAsF₆ + PMDT in a 30:70 mole percent mixture of TMSO:toluene (60, 61).

In eq. [18] A is a constant, T_0 is the ideal glass transition temperature closely related to the glass transition temperature T_g as measured by differential scanning calorimetry (DSC), and E is the activation energy. The activation energy E can be interpreted either in terms of configurational entropy theory or free volume theory (66) and hence relates to the segmental motion of the polymer chains. The magnitude of σ is an indication of the maximum power that can be obtained from a given lithium cell whereas the ion transference number of Li^+ will determine the maximum limiting current that can be drawn. In aprotic organic solvents in which lithium salts are highly soluble due to strong interaction with an ether or carboxyl oxygen, values of t_+ are generally well below the desired value of 1.0 (e.g., see Table 5), and in solid state polymer systems, values of t_+ are generally less than those in aprotic solvents. Thus considerable effort is presently being expended in the development of polymers which exhibit high values of t_+ for lithium. Recent studies on gel systems employing poly(methylmethacrylate) (67) and polytetrahydrofuran (68) polymer hosts are examples of recent research which report ionically conducting polymer gels with lithium ion transport numbers exceeding 0.5; by optimizing both the nature of the plasticizer and salt, t_+ values of 0.5 to 0.7 were achieved.

Polyethylene oxide (PEO), $[-\text{CH}_2\text{CH}_2-\text{O}-]_n$, is the host polymer that has received the most attention up to the present, but because of its crystallinity, segmental motion responsible for Li^+ ion transport is restricted which limits the application of PEO-based systems to temperatures around 100°C; room

temperature conductivities are of the order of $10^{-8} \text{ S cm}^{-1}$. Many attempts have been made to modify PEO systems to increase the amorphous (conducting) regions of this host polymer such as synthesizing copolymers of PEO with flexible backbone polymers such as polysiloxanes (69) and polyphosphazenes (70). These attempts to produce amorphous polymers have been successful, but still the conductivities of these systems are somewhat low being of the order of $10^{-5} \text{ S cm}^{-1}$ at best. An alternative approach first proposed by Feaullade and Perche in 1975 (71) utilizes addition of plasticizers, nominally electrolyte solutions which are trapped or immobilized in polymer matrices. Host polymers which are presently receiving considerable attention for this approach are polyacrylonitrile (PAN), $[-\text{CH}_2\text{CH}_2(\text{CN})-]_n$, poly(vinylidene) difluoride (PVDF), $[-\text{CH}_2\text{CF}_2-]_n$, and poly(methyl methacrylate), (PMMA), $[-\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)-]_n$. Methods used to immobilize liquid electrolytes in a polymer include UV crosslinking, gelification and casting, and the resulting materials are commonly referred to as polymer gels, hybrid electrolytes or gelionics (37). Using this approach, the conductivities of these polymer gels can approach that of the liquid electrolyte used as the plasticizer as shown in Fig. 13 (72). In this figure, the temperature behavior of several

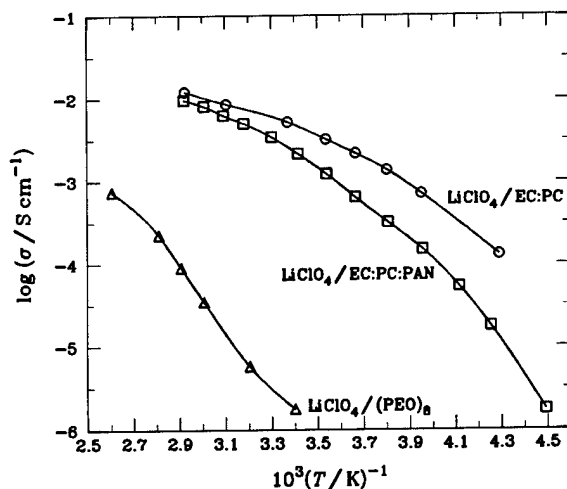


Figure 13. Arrhenius plots of conductivity of LiClO_4 (1) in a PAN gel with the same LiClO_4 content as that that for (2) the reference liquid electrolyte, and (3) in PEO. See text for the molar molar compositions of these systems.

polymer electrolytes is compared to that of an equimolar mixture of liquid EC-PC in which LiClO_4 is used as the electrolyte. The molar ratio of solvent (EC + PC) to that of LiClO_4 is 8.8 to 1.0 (70). This same electrolyte used as the plasticizer in a PAN gel of composition 38 mol % EC, 33 mol % PC, 21 mol % PAN and 8 mol % LiClO_4 is seen in this figure to exhibit conductivities ($1\text{--}2 \cdot 10^{-3} \text{ S cm}^{-1}$) which are reasonably close to that of the pure liquid. The temperature dependence of κ for LiClO_4 in PEO (mol composition corresponds to 8 PEO oxygens per Li) is also included in this

figure to dramatize the ambient temperature conductivity advantage of the polymer gel. As in the cases discussed above for liquid electrolytes, ion aggregation is also a problem in polymer gels (probably more so), and it is therefore expected that the nature of the anion will have an effect on the conductivity of the gel. This effect for PVDF gels is significant as seen in Fig. 14 (from ref.

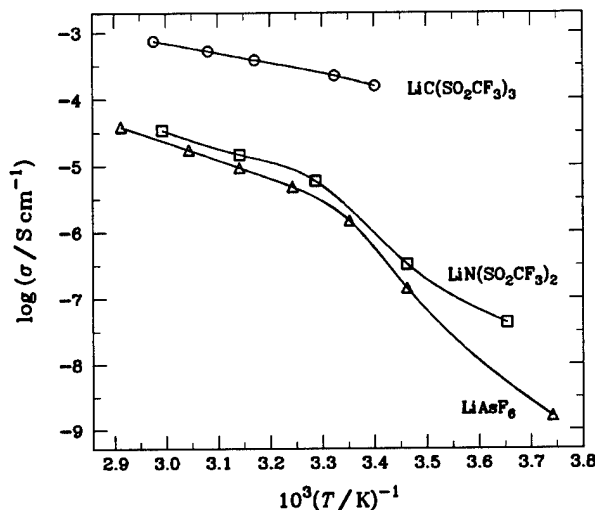


Figure 14. Arrhenius plots for PVDF polymer gels comparing LiAsF_6 , $\text{LiN(SO}_2\text{CF}_3)_2$ and $\text{LiC(SO}_2\text{CF}_3)_3$. Molar compositions of the gels are:
 (A) 36.3 % PVDF, 35.8 % PC, 18.5 % DMF, 6.1 % DEP and 3.3 % LiAsF_6 .
 (B) 36.7 % PVDF, 36.2 % PC, 18.8 % DMF, 4.9 % DBF and 3.4 % imide.
 (C) 36.7 % PVDF, 36.2 % PC, 18.8 % DMF, 4.9 % DBF and 3.4 % methide.

(73)). The plasticizing solutions used in this study (ref. 73) are based on PC-DMF mixtures with either diethylphthalate (DEP) or dibutylphthalate (DBF), and compositions of these gels are given in the caption to Fig. 14. The reasons why the conductivities of the methide based gels are greater than for the other gels are not well understood at this time, but we believe it to be due, in part, to an enhanced plasticizing effect by the methide salt itself. We base this conclusion on our DSC measurements in which the following glass transition temperatures, T_g , were found for these gels: $T_g = -60.0^\circ\text{C}$ for the arsenate gel, $T_g = -76.0^\circ\text{C}$ for the imide gel, and $T_g = -83.1^\circ\text{C}$ for the methide gel.

As in several instances for liquid electrolytes (see above discussions), the addition of macrocyclic ligands such as cryptands and crown ethers to SPEs have also been found to increase the conductivities of these systems (74-76). This is another area for future research which we believe will be fruitful.

In the section on ANODES above, the problem of corrosion of metallic Li and Li_xC_6 anodes was discussed for liquid electrolytes. The same problem exists at the lithium - polymer electrolyte

interface, but may be somewhat more severe since continued buildup of the passive layer formed during successive discharge and charge cycles can result in physical detachment of large areas of the polymer electrolyte from the anode surface. An effective approach towards the solution of this problem was reported in (37, 77-79) where it was found that addition of ceramic materials such as zeolites and γ -LiAlO₂ results in polymers with greater mechanical stability, increased conductivity and increased anode-polymer interface stability. For example, Capuano et al. (77) found additions of up to 10 mass % γ -LiAlO₂ or Al₂O₃ to LiClO₄(PEO)₈ increased the conductivity by an order of magnitude and significantly enhanced the interfacial stability. An example of this effect for a PAN gel is shown in Fig. 15 which reports the change in this interfacial resistance as a function of time

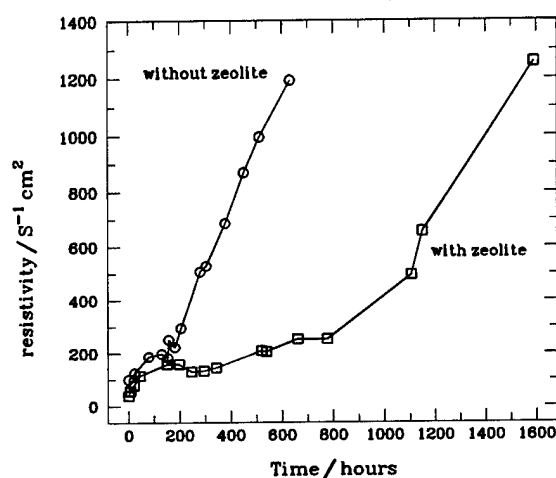


Figure 15. Time evolution of the interfacial resistance, R_i , of the lithium electrode in contact with LiClO₄-PC-EC-PAN with (□) and without (O) zeolite additions.

with and without the zeolite (Na₁₂[Al₁₂Si₁₂O₄₈]). These observed beneficial results are attributed to a combination of effects which include reducing the crystallinity (i.e., increases the volume of the amorphous phase) in PEO-based polymers and action as an impurity getter in gel-type polymers.

Rocking chair cells and batteries based on carbon anodes and solid polymer electrolytes have distinct advantages over those based on liquid electrolytes as discussed above (e.g. safety, economics, ease of manufacturing in almost any physical shape desired). The key areas required for meeting those objectives given in Table 1 are those related to conductivity over a wide temperature range, increasing the lithium ion transport number, and diminishing the corrosion at the anode-polymer interface. Progress in these areas is encouraging, and we anticipate that in addition to liquid electrolyte systems, these all solid state systems will also play an important role in future mobile energy sources.

CONCLUSIONS

There is no doubt that rechargeable lithium batteries will play an important role for future portable electronic devices and probably for vehicular traction. Environmental concerns almost require the elimination of cells and batteries containing lead, mercury and cadmium, and the question remains as to which battery chemistries will replace these conventional aqueous systems. The various possibilities discussed in the present review indicate that a number of problems with rechargeable lithium batteries are still to be resolved, but we are confident that continued basic research, in combination with advanced development, will lead to success.

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